

Charge redistribution at Pd surfaces: *ab initio* grounds for *tight-binding* interatomic potentials

S. Sawaya, J. Goniakowski, C. Mottet, A. Saúl and G. Trégliá

CRMC2, Centre National de la Recherche Scientifique*, Campus de Luminy, Case 913, 13288 Marseille CEDEX 9, France.
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A simplified *tight-binding* description of the electronic structure is often necessary for complex studies of surfaces of transition metal compounds. This requires a self-consistent parametrization of the charge redistribution, which is not obvious for late transition series elements (such as *Pd*, *Cu*, *Au*), for which not only *d* but also *s* – *p* electrons have to be taken into account. We show here, with the help of *ab initio* FP-LMTO approach, that for these elements the electronic charge is unchanged from bulk to the surface, not only per site but also per orbital. This implies different level shifts for each orbital in order to achieve this **orbital neutrality** rule. Our results invalidate any neutrality rule which would allow charge redistribution between orbitals to ensure a common **rigid shift** for all of them. Moreover, in the case of *Pd*, the power law which governs the variation of band energy with respect to coordination number, is found to differ significantly from the usual *tight-binding* square root.

I. INTRODUCTION

Transition metal materials are widely studied due to their remarkable properties in various domains such as metallurgy, electronics, magnetism or catalysis. These properties can be related to the particular electronic structure of transition metals, characterized principally by the progressive filling (up to ten electrons) of a narrow *d* band. However, when this band becomes nearly filled (i.e. for elements at the end of the transition series) the role of external *s* and *p* electrons can no longer be neglected. Therefore, any relevant theoretical treatment requires to account simultaneously for the two different types of electronic states: *s* and *p* electrons with strong itinerant character, and *d* electrons with partially localized one. Such treatments involve, depending on the problem, two different types of methods, of opposite complexity and flexibility. On the one hand *semi-empirical* methods, which require fitted parameters but can be applied to large systems (a few thousands of atoms) with complex atomic (defects, surfaces) or chemical (alloys) structure. On the other hand *ab initio* methods, which do not need any parameters but are limited to small systems of only a few tenths of atoms. Now, the modern challenge in material science is to predict both the atomic and chemical structure of complex systems (such as alloy surfaces) from the only knowledge of the electronic structure of their components. This requires large scale kinetic simulations of the Monte Carlo or Molecular Dynamics type, in the framework of interatomic potentials which have to be as simple as possible (i.e. preferably in analytical form) while remaining fine enough to describe correctly differences in metallic cohesion of elements. In particular, one has to go beyond simple pair interaction potentials, which have proven to be inadequate for transition metals. Appropriate potentials can be obtained from semi-empirical electronic structure calculations, suited to the character of the electrons involved: *effective medium*

theory for *s* – *p* electrons¹, *embedded atom model*² or *tight-binding* approximation³ for *d* electrons. More precisely, in the framework of *tight-binding* approximation, different types of potentials have been derived, depending on the type of addressed problem: *second moment many-body* potentials for atomic relaxations⁴ or *effective pair-wise* potentials for ordering processes in alloys⁵. However, it is worth noticing that these potentials have been obtained under drastic assumptions concerning the charge redistribution close to the surface (or more generally, close to a defect). In particular, the commonly admitted rule is that of local charge neutrality at the defect. Let us emphasize that infringing this law can change completely the essential features of the simplified models mentioned above. It is thus essential, to validate the semi-empirical potentials in use, or to propose alternative ones, starting from some parameter-free reference calculations and deriving general trends for the variation of charge transfer near the defects as a function of coordination and of *d* band filling.

Beyond these applications which only require an overall knowledge of the local density of states since they involve integrated quantities (energy, band filling), a precise knowledge of the local densities is needed for direct comparison with experiments (angular photoemission) or for properties related to details of the density of states near the Fermi level (reactivity, magnetism). The *tight-binding* formalism is in general sufficient to account for these requirements as long as *d* electrons play the predominant role, i.e. for not too large *d* band filling³. The problem becomes complicated for elements belonging to the end of transition series (which are the most commonly used for their catalytical (*Pd*) or magnetic (*Ni*) properties). The *d* band of these elements is nearly filled so that the role of *s* – *p* electrons can no longer be neglected. But an unified description of *s* – *p* and *d* electrons is tricky since the strong itinerant character of the former deserves nearly free electron approaches while the less delocalized

character of the latter is the basis of the *tight-binding* approximation. In spite of this apparent incompatibility, it is commonly admitted that one can take into account the $s - p$ and d hybridization in the framework of the *tight-binding* approximation⁶. However, this implies to extend the local neutrality rules near the defects, previously used for d orbitals only, to the case where orbitals of different character are involved. It is then essential, before using extensively this type of approach, to analyze the assumptions in the light of *ab initio* calculations in which both $s - p$ and d electrons are treated on the same footing.

We touch here an aspect of a more general problem of transferability of tight-binding parameters to a new environment and of conditions these parameters should meet in order to describe the electronic structure of modified atomic and chemical configurations which can occur in actual materials. More precisely, they should remain valid in a wide range of atomic coordinations and environments, apply over a range of interatomic separations and describe accurately the chemical effects between unlike species. It is thus essential to examine them in the light of *ab initio* type calculations, considered as exact reference. Several attempts have already been made to check the reliability and usefulness of these tight-binding parameters by examining their transferability with changes in structure⁷⁻⁹ and chemical environment¹⁰. However, at present only few studies can be found on what concerns the influence of the modified surface environment on the $sp - d$ hybridization and induced $sp - d$ charge transfers.

Therefore, the aim of the present paper is to review, following a similar approach, the alternative hypothesis underlying the semi-empirical methods as applied to transition metals of the end of the series and to validate some simple rules to be used in *tight-binding* approaches. In order to do this we analyze the variation of the local electronic structure (site projected densities of states, level shifts, charge transfer) from bulk to low index surfaces of Pd obtained within a parameter-free, FP-LMTO approach. We then derive the general trends and use them as to modify accordingly the *tight-binding* framework. The paper is organized as follows: in the Section II we present to some extent the principles of the *tight-binding* approach and the question marks on the parametrization one has to answer. Section III is devoted to a brief description of the FP-LMTO method which we have chosen for the reference calculations. In Section IV we outline our *ab initio* results and compare them to results obtained within *tight-binding* approach based on alternative neutrality rules. We discuss their respective similarities and differences as well as general tendencies which can be due to application of this or the other assumption.

II. TIGHT-BINDING TREATMENT

We will use in the following the usual *tight-binding* hamiltonian extended to the case of multiple orbitals :

$$H = \sum_{i,\lambda} |i, \lambda \rangle \epsilon_{i\lambda}^0 \langle i, \lambda| + \sum_{\lambda\mu, i \neq j} |i, \lambda \rangle \beta_{ij}^{\lambda\mu} \langle j, \mu| \quad (1)$$

It involves two types of parameters:

- $\epsilon_{i\lambda}^0 = \epsilon_{\lambda}^0 + \delta\epsilon_{i\lambda}$: where ϵ_{λ}^0 is the atomic level for the orbital λ (s , p , d), and $\delta\epsilon_{i\lambda}$ is the shift of the atomic level for orbital λ at site i , which is required to achieve the charge self-consistency on any site i which is not equivalent to a bulk site (surface, defect)¹¹.
- $\beta_{ij}^{\lambda\mu}$: hopping integral between the orbital λ at site i and the orbital μ at site j

These hopping integrals can be expressed in terms of the usual Slater parameters. They will be derived here from the band structure using the interpolation scheme developed by Papaconstantopoulos¹².

The local densities of states $n_{i\lambda}(E, \delta\epsilon_{i\lambda})$ are obtained from the continued fraction expansion of the Green function $G(E) = (E - H)^{-1}$, the coefficients of which are directly related to the first moments of the density of states, and calculated within the *recursion* method¹³. It is then possible to define the band filling per orbital $N_{i\lambda}$, which is obtained by integration of the partial local density of states up to the Fermi level E_F :

$$N_{i\lambda} = \int_{-\infty}^{E_F} n_{i\lambda}(E, \delta\epsilon_{i\lambda}) dE. \quad (2)$$

Total band filling (number of valence electrons) can be obtained by summing over all orbitals $N_i = \sum_{\lambda} N_{i\lambda}$.

The problem is then to calculate the level shift $\delta\epsilon_{i\lambda}$ corresponding to the charge self-consistency on defect sites. When only the d electrons need to be taken into account (elements in the middle of transition series), it has been shown¹⁴ that the charge self-consistency reduces to a *local charge neutrality condition*. According to this condition, number of d electrons on a defect site (surface) is the same as on the bulk site. In other words, whatever the site i , $N_{id} = N_{bulk,d}$. Then, all the inner levels are assumed to follow rigidly this valence d -band shift, giving rise to surface core level shifts evidenced by photoemission experiments¹¹. The situation is more intricate when orbitals of different character have to be taken into account. Actually, one can then wonder if a similar local neutrality rule still applies ($N_i = N_{bulk}$), and if so has it to be achieved for each of orbitals separately ($N_{i\lambda} = N_{bulk,\lambda}$) or not ($N_{i\lambda} \neq N_{bulk,\lambda}$)?

- If it is true ($N_{i\lambda} = N_{bulk,\lambda}$), one should then introduce three different level shifts ($\delta\epsilon_{is} \neq \delta\epsilon_{ip} \neq \delta\epsilon_{id}$) to ensure each orbital neutrality.

- If it is not true, i.e. that a charge redistribution occurs between the different orbitals ($N_{i\lambda} \neq N_{bulk,\lambda}$), then the neutrality rule contains too much degrees of freedom, and we have to introduce additional assumptions on the shifts. A usual one is then to follow the rule for inner shell and to impose a common **rigid** shift for all orbitals⁶ ($\delta\epsilon_{is} = \delta\epsilon_{ip} = \delta\epsilon_{id}$).

The choice is far from being harmless as will be seen in section IV. If one remembers that these are quantities which are closely related to reactivity (adsorption energies) or magnetic properties, one has to be able to decide which approximation approaches better the reality. One solution would be to compare these results to experimental data, for instance to the values of the core level shifts. However, this is not completely unambiguous, since the respective influence of initial and final state effects cannot be precisely estimated. The best way to proceed is then to perform some *ab initio* calculation leading to the full charge distribution, and to analyze how it can be shared between different sites and different types of orbitals.

III. LMTO METHOD

To perform these reference parameter-free calculations we have chosen a LDA based FP-LMTO method^{15,16}. It has proven to be well suited for the description of bulk electronic structure of transition metal compounds^{17,18}, and no approximation on shape of charge density nor potential makes it also adequate for low symmetry systems such as surfaces^{19,20}.

Within the FP-LMTO method the space is divided into non-overlapping spheres centered on atomic sites. The basis set consists of atom-centered Hankel envelope functions which are augmented inside atomic spheres by means of numerical solution of scalar-relativistic Dirac equation. Due to the non vanishing interstitial region it is enough to use the minimal basis set - we have used three *s*, three *p* and three *d* functions per atomic site (for three different energies: -0.7, -1.0 and -2.3 Ry)¹⁹ corresponding to three different localization of Hankel envelopes. We have used 'two-panel' technique as to include 4*p* semicore electrons as full band states. Valence band contains 4*d*, 5*s* and 5*p* states.

To obtain an accurate representation of the exponentially decaying density outside the surface, in slab calculations it is necessary to cover the surfaces with one or two layers of empty spheres. We have included spheres which are the first neighbors of surface metal atoms. One layer of empty spheres was thus used on (111) and (100) faces and two layers on the more open (110) face. The empty-sphere angular-momentum cutoff for charge density and for the augmentation of the wave function was fixed to 6 and 4, respectively.

We have assured ourself that the basic experimental bulk characteristics of palladium are reproduced correctly (with respect to measured values: lattice paramete-

ter -1%, bulk modulus 10%, cohesive energy 20% - overestimation of the latter is however one of well known deficiencies of the LDA). The lattice constant determined for the bulk was systematically used for slab calculations. Surface relaxation effects were not taken into account. We have tested the convergence of results with respect to the slab thickness (in order to obtain bulk-like properties in the center of the slab) using as a criterion the modifications of calculated surface energy. Increasing the number of layers from 9 to 11 changes the latter by less than 40 meV per surface atom. Nine layer slabs were thus adopted for the calculations.

The **k** point sampling of the Brillouin zone was done with special point meshes and converged to within 50 meV/atom (with the Gaussian broadening of 20 mRy) for 126 **k** points in the irreducible part of BZ for (100) surface, 216 **k** points for (110) and 226 **k** for (111).

IV. RESULTS AND DISCUSSION

Before presenting our results, it is worth noticing that we have performed calculations for various FCC metals belonging either to the end of the transition metal series (*Pd*, *Ni*) or to the noble metal column (*Cu*, *Ag*, *Au*) for which the role of *s-p* electrons is yet much predominant. Since the essential results are the same for all these elements, we will only present here the case of *Pd*, which is likely the element which has been the most widely studied in relation with its unique catalytical properties. In order to use the conclusions of the *ab initio* calculations as a ground for the *tight-binding* description of surfaces we need to start by checking if both methods lead to similar results for the bulk electronic structure. Having a look at Figure 1, where we have plotted the bulk LDOS calculated with the two approaches one can see that the structure of *tight-binding* bulk LDOS is in good agreement with the corresponding *ab initio* results, provided that the former one is calculated with a sufficiently large number of exact moments. Here a number of eighty has been used in order to reproduce all the details of the *ab initio* LDOS. The comparison between the dotted curves in Figure 1 show that the interpolation scheme is correct and that, at least in the bulk, *tight-binding* formalism can be successfully applied to describe elements of the end of the transition series, by taking into account not only valence *d* states but also *s-p* ones.

The situation is obviously more complex at a surface. As explained in Section II, in order to propose a *tight-binding* self-consistent calculation scheme, one has to know how the electronic charge distribution on the surface differs from that in the bulk. Indeed, the knowledge of the charge transfers is required to write the charge self-consistency rule which will then allow us to determine, using an iterative scheme, the level shifts: $\delta\epsilon_{i\lambda}$. We have thus analyzed the spacial redistribution of electrons due to surface creation, as obtained within the FP-LMTO ap-

proach. In Figure 2 we plot, for two surface orientations ((111) and (100)), a contour map of the difference between valence electron densities obtained respectively for slab and bulk geometries, cross-sectioned along a plane perpendicular to the surface. It can easily be seen that the overall modifications are very small. They are principally constrained to within the surface atomic layer and consist of polarization of surface atoms related to depopulation of orbitals pointing into vacuum. On the other hand, some electrons are spilled out into the vacuum region corresponding to hollow surface sites.

In order to quantify these effects better, we give in Table I the charge distributions calculated inside (s , p and d orbitals) and outside (interstitial region and hollow surface sites) the atomic MT spheres, for atoms on surfaces of three inequivalent orientations and, for the sake of comparison, in a bulk plane. The electronic occupation for atoms in the first underlayers are not given since they are found to be quasi-identical to those in the bulk. Separation into the two regions (inside and outside the spheres) avoids any arbitrary reattribution of interstitial electrons to particular atomic sites. However, when trying to reproduce the above charge distribution with the *tight-binding* approach, we will have to remember that its basis set is not conceived as to represent off-site charges. The only solution will then be to reattribute electrons found in the hollow surface sites to some on-site atomic orbitals. Due to spacial asymmetry and to their relative delocalization with respect to surface atoms, these are the p orbitals that seem to be the most adequate candidates. This means that, for the p charge distribution, we would add the charge found in the hollow sites to that of the p -orbital. Once the electrons reassigned in this way, one can see that the differences between surface and bulk distributions are indeed very small. The electron transfer is even less pronounced than in the contour plot, because it is integrated over orbitals of the same character: on-site electron transfer between d orbitals of different orientations, which can be seen in the plot, does not influence s , p and d - projected electron occupations.

As a conclusion, one can say that the self-consistent treatment of the charge at a surface of a system with $sp-d$ hybridization can be reduced to a condition of local charge neutrality **per orbital**. It is worth noting that this condition is not compatible with the rigid shift $\delta\epsilon_i$ used in old scheme⁶.

Let us now see to what extent a *tight-binding* calculation, based on this condition of charge neutrality per orbital, indeed reproduces correctly the *ab initio* results. To this aim, we first compare, in Figure 1, the LDOS for (111) and (100) surface sites calculated by either the *tight-binding* approach (Fig.1b-1b') or the FP-LMTO method (Fig.1a-1a'). One can see that the overall deformation induced by the surface is well reproduced in this framework. In order to make the comparison more quantitative we have looked on basic characteristics of surface bands. In particular we have compared the first moment of LDOS, related directly to the surface level

shift. As can be seen in Table II, both *ab initio* and *tight-binding* calculations predict an upward surface level shift, smaller for compact (111) surface and enhanced for the most open (110) one. The values are found in good agreement: they should now deserve some experimental confirmation from core level spectroscopy or from surface adsorption energies.

In order to illustrate how crucial it is to achieve properly this charge self-consistency, we have also performed the *tight-binding* calculation by assuming, as in some previous works⁶, that at the surface the charge can be redistributed between the different orbitals, and that the latter undergo the same rigid level shift. Comparing the LDOS obtained in this way (see Fig.1c-1c') to the previous ones (see Fig.1b-1b') is meaningful. Indeed, the detailed structure and position of peaks in the LDOS are different, in particular around the Fermi level and in the bottom of the band, where the $sp-d$ hybridization is the most important. This could have been expected since the structure of the bottom of the band is very dependent on the respective positions of the levels for s , p and d orbitals. The comparison between these curves and the *ab initio* ones (see Fig.1a-1a') shows a significantly better agreement for those obtained by assuming orbital charge neutrality than a common rigid shift. This conclusion can be made more convincing by comparing the surface level shift. Indeed, as can be seen in Table II, one still recovers, within the rigid shift assumption, an upward surface level shift, with the same trend from the compact to the open surface, but with a significantly too low value, which can be attributed to an over-estimated electron transfer from s and p to d orbitals on sites of reduced coordination.

One can then conclude that the fundamental difference induced by alternative neutrality conditions underlying the *tight-binding* approach is the way the s and p electrons are transferred to d orbital when the coordination number decreases. Although in the atomic limit of Pd all electrons are to be found in the d shell, the approach which allows charge redistribution predicts strong transfers already for relatively high coordination numbers. Our FP-LMTO results suggest that this is not the case and that a constant band-filling (orbital neutrality) corresponds better to calculated trends. However, the limits of applicability of the orbital neutrality condition for very low coordination number are not still unambiguously defined.

Finally, it is interesting to compare also the values of the second moments μ_2 (i.e. the bandwidth at half-maximum) of the *tight-binding* d -LDOS obtained for the bulk and three different surface orientations ($Z = 12, 9, 8, 7$), to those derived from LMTO calculations. Indeed, a precise knowledge of the variation of μ_2 with the coordination number (Z) is essential when interested in the definition of simple many-body interatomic potentials to be used in numerical simulations. In particular, this could give us an alternative to the so-called *second moment* approximation⁴, in which the attractive part (E_b)

of the potential is fitted to the band energy of a rectangular density of states, of same second moment as the actual density of states. This constraint leads to:

$$E_b \sim \mu_2^{1/2}. \quad (3)$$

The problem is then to calculate this second moment.

In the *tight-binding* approximation, it is known to be linear in the effective coordination number:

$$\mu_2^{TB} \sim Z, \quad (4)$$

so that the Eq.(3) can be re-written:

$$E_b^{TB} \sim Z^{1/2}, \quad (5)$$

which leads to the usual *square-root* many-body character of this potential⁴. However, in spite of its overall success, this potential sometimes fails to reproduce the experimental variation of the energy as a function of the coordination number in the whole Z -range, in particular for very low values of Z . This is in particular the case for Pd ²¹. The alternative is then:

- either to go beyond the second moment approximation to account for details of the LDOS which are obviously neglected when using a rectangular shape,
- or to stay within such a second moment approximation, provided that one calculates the second moment as accurately as possible, going beyond the *tight-binding* approximation by using *ab initio* calculations.

The first solution has already been explored, but without $sp-d$ hybridization, by other authors²², leading to $E_b^{TB} \sim Z^{2/3}$. We will then illustrate here the consequences of choosing the second solution. In that case, deriving μ_2 from our LMTO calculations. Indeed, this leads to:

$$\mu_2^{LMTO} \sim Z^{3/2}, \quad (6)$$

which, used in the eq.(3), gives a somewhat different Z -dependence for the attractive term:

$$E_b^{LMTO} \sim Z^{3/4}. \quad (7)$$

This means that a proper treatment of $sp-d$ hybridization leads to a dependence of the band term which is intermediate between the square-root ($E_b \sim Z^{1/2}$) and a pairwise ($E_b \sim Z$) dependence. Actually, this result seems to be confirmed in the particular case of Pd , for which the experimental variation of the energy with coordination number is found to be almost pairwise. However, it is worth pointing out that, contrary to our conclusions concerning charge neutrality, this result is not general and should be actualized for each different element.

V. CONCLUSION

As a conclusion, comparison of calculated characteristics of the electronic structure obtained within an *ab initio* FP-LMTO method and within a semi-empirical *tight-binding* approach shows that it is still legitimate to treat the surfaces of elements of the end of the transition series such as Pd with the latter. However one has to take care that the $sp-d$ hybridization is correctly taken into account. To this aim, one has to achieve the proper neutrality condition underlying the *tight-binding* approach to compact surfaces. What we learn from the above *ab initio* calculations is that the electronic occupation of orbitals does not depend on the environment. Under this assumption, it is therefore possible to apply all the conclusions obtained for systems with only d electrons, and in particular to use the simplified potentials developed to treat either morphology and dynamics (*second moment approximation*) or surface segregation (*tight-binding Ising model*).

* The CRMC2 is also associated to the Universities of Aix-Marseille II and III.

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	<i>Pd(bulk)</i>	<i>Pd(111)</i>	<i>Pd(100)</i>	<i>Pd(110)</i>
N_s	0.39	0.37	0.35	0.34
N_p	0.34	0.25	0.22	0.19
N_d	8.09	8.12	8.14	8.16
<i>Interstitial</i>	1.18	1.13	1.12	1.05
<i>Hollow sites</i>		0.13	0.17	0.26
<i>Total</i>	10.00	10.00	10.00	10.00

TABLE I. Orbital projected charge distribution inside the MT sphere (*s*, *p*, *d* orbitals) and outside (either in the interstitial region or in the hollow surface sites), calculated within FP-LMTO approach.

	<i>Pd(111)</i>	<i>Pd(100)</i>	<i>Pd(110)</i>
<i>FP – LMTO</i>	0.38	0.54	0.63
<i>T.B. : orbital neutrality</i> ($\delta\epsilon_{is} \neq \delta\epsilon_{ip} \neq \delta\epsilon_{id}$)	0.36	0.55	0.64
<i>T.B. : orbital charge redistribution</i> ($\delta\epsilon_{is} = \delta\epsilon_{ip} = \delta\epsilon_{id}$)	0.17	0.18	0.25

TABLE II. Surface level shift $\delta\epsilon_{id}$ (eV) for *d* orbitals on three inequivalent surfaces deduced from *FP – LMTO* calculations and calculated with *tight-binding* approach (*T.B.*) based on alternative neutrality hypothesis

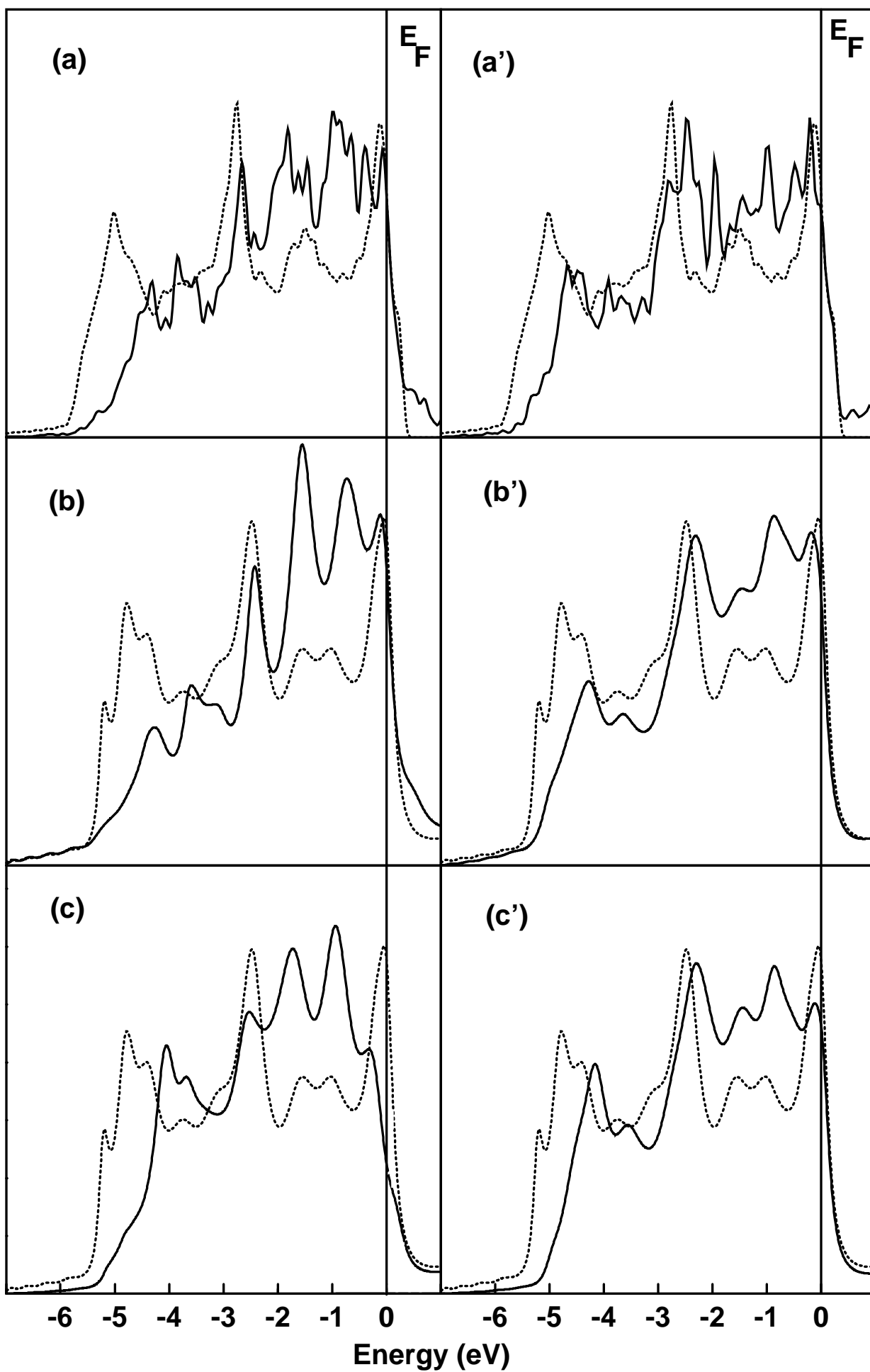
FIG. 1. *Pd* bulk (dotted curve) and surface (full curve) local densities of states for two orientations: (100) (left hand side) and (111) (right hand side). (a)-(a'): FP-LMTO calculation, (b)-(b')*tight-binding* assuming an orbital charge neutrality rule, (c)-(c')*tight-binding* assuming orbital charge redistribution and a rigid level shift.

FIG. 2. Contour map of the *excess* electronic density $\Delta n(r) = n_s(r) - n_b(r)$. $n_s(r)$ is the actual electronic density calculated for the slabs geometries and $n_b(r)$ the one calculated replacing all the atoms of the slabs with bulk ones. The figures represent surface cuts perpendicular to the (100) (left hand side) and (111) (right hand side) surfaces. A grey scale proportional to $\Delta n(r)$ was used, white corresponds to the minimum negative value and black to the maximum positive one.

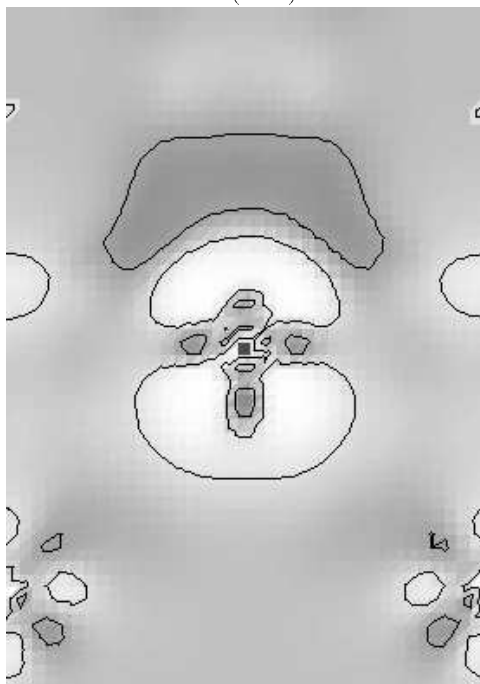
Density of states (arb. units)

(100)

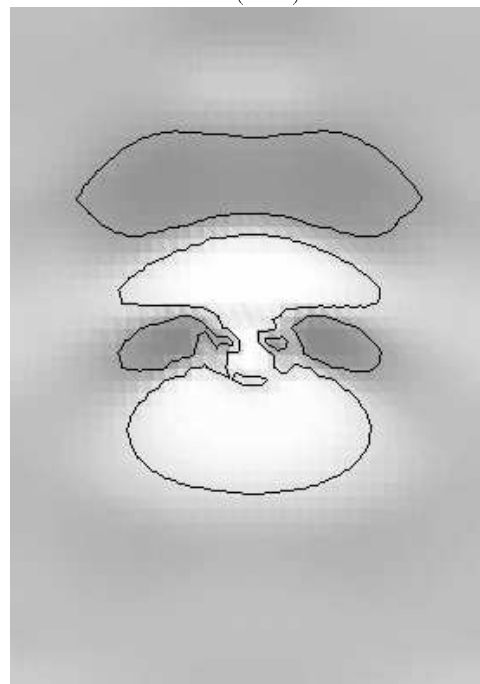
(111)



Pd(100)



Pd(111)



-- Pd0 --

<- Pd1 - - -

- - - Pd1 ->